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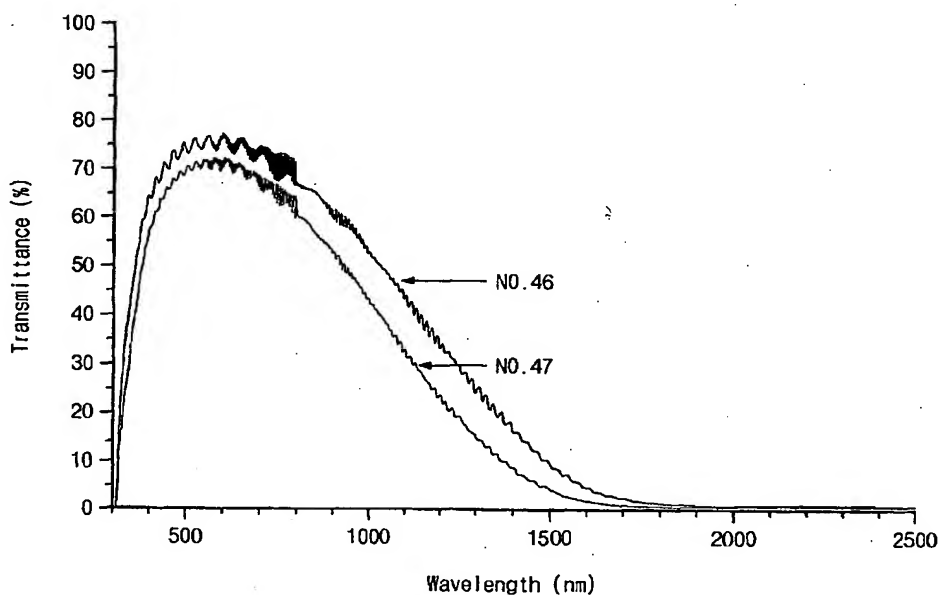
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(54) Title: COMPOSITION FOR CUTTING OFF HEAT-RAY, FILM FORMED THEREFROM AND METHOD FOR FORMING THE COMPOSITION AND THE FILM



(57) Abstract: Disclosed are heat-ray cutoff compounds, films and method using them. The heat-ray compound is produced by dispersing conductive nanoparticles in an amphoteric solvent with acids and dispersion sol, which provides a low cost production for the heat-ray cutoff films because it is able to any resin binder without sorting the kinds of resin binders (hydrolic or alcoholic, or anti-hydrolic).

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## Title of Invention

COMPOSITION FOR CUTTING OFF HEAT-RAY, FILM FORMED THEREFROM AND  
METHOD FOR FORMING THE COMPOSITION AND THE FILM

## 5 Technical Field

The present invention relates to compositions for cutting of heat rays, and more particularly, to compositions for cutting off heat rays with being compatible with hydrolic or alcoholic and anti-hydrolic resin binder, films formed therefrom, and methods of forming them.

10

## Background Art

Transparent films effective in screening heat is advantageous to be associated with means for preventing malfunctions of integrated circuits or electronic components, or for reducing the costs for cooling and heating by lessening the amount of solar energy going in and out of rooms and automobiles through windows. In addition, it is possible to offer effects of screening infrared rays when they are applied to various products such as optical fibers, sun visors, PET vessels, packaging films, glasses, textile goods, peep holes of heaters, heating apparatuses, and so on.

20

There has been proposed several films, which is capable of transmitting light with the wavelength of 380 ~ 780 nm in a visible right range while reflecting light with the wavelength of 800 ~ 2500 nm around the range of infrared rays, formed by the methods of: (1) forming a film with ingredients of tin oxide and antimony oxide by means of a spray process (refer to JP03-103341); (2) forming a film of tin-doped indium oxide (hereinafter, "ITO") on a glass substrate by means of physical vapor deposition, chemical vapor

25

deposition, or sputtering; and (3) coating an near-infrared absorber in the type of organic dyestuffs, such as pthalocyanine series, anthraquinone series, naphthoquinone series, cyanine series, naphthalocyanine series, condensed azo polymers, and pyrrol series, on a substrate by means of an organic solvent and  
5 an organic binder, or transform the about-infrared absorber into a coating.

However, the method (1) needs a thick film because it has weak performance for screening heat rays, resulting in a low transmittance rate for visible light. The method (2) consumes a high product cost because it needs an apparatus with control of the atmosphere in high vacuum and accuracy, being  
10 restricted in sizes of coating films and shapes and disadvantageous to implementation due to insufficient mass-productivity. The method (3) is insufficient in advancing the heat cutoff efficiency because it has a low transmittance rate for visible light and dark colors and is restricted to absorb near-infrared rays with wavelengths 690 ~ 1000 nm. While the methods (1)  
15 and (2) are available to cut off ultraviolet rays as well as heat rays, they are incapable of receiving electric waves from mobile phones, televisions, or radios, because their materials reflects the electric waves due to small surface resistance, i.e., high electrical conductance.

In order to overcome the problems, there have been proposed several  
20 techniques disclosed in Japanese Patent NOs. JP56-156606, JP58-117228, and JP63-281837, in which respectively an antimony-doped tin oxide (hereinafter, referred to as "ATO") is mixed with a resin binder, ATO is directly added to a resin binder dissolved in an organic solvent, and a coating compound manufactured by adding an organic binder and tin oxide nanoparticles into a

splittable surfactant is deposited to form a heat-ray cutoff film. But it still needs a thick film enough to perform an infrared ray cutoff function, which contains low transmittance rate for a visible light to lower the transparency.

On the other hand, Japanese Patent NOs. JP07-24957, JP07-70363, JP07-70481, JP07-70842, JP07-70445, and JP08-41441 disclose the methods in which;  
5 a powder with an excellent performance of screening heat rays is made by processing or manufacturing ITO nanoparticles in the atmosphere of inert gas; and a heat cutoff film formed by mixing organic/inorganic binders with a dispersion sol made from using water or an alcoholic solvent without using an  
10 organic solvent, capable of screening heat rays over 90% under the condition of wavelength 100 nm. However, as the ITO nanoparticles is ingredient of a highly expensive indium and obtained by processing twice in the atmosphere of inert gas, it is limited in practical implementation due to the high product cost. Moreover, the ITO nanoparticles cause delamination or cohesion when they are  
15 mixed with a ultraviolet-hardening resin binder and is in poor preservation.

Japanese Patent NOs. JP09-324144, JP09-310031, JP09-316115, JP09-316363, JP10-100310, and JP12-169765 propose the method of mixing a dispersion sol of the first heat-ray cutoff nanoparticles and the second heat-ray cutoff compound (the near-infrared absorber or 6-boronic nanoparticles), or  
20 mixing respective coating compounds. However, in this case, it has disadvantages that a visible ray transmittance rate is remarkably degraded or it is not easy to induce dispersion while manufacturing a dispersion sol of the second heat-ray cutoff compound, which disables a low cost mass-production for the heat-ray cutoff films.

Japanese Patent NOs. JP06-262717, JP06-316439, JP06-257922, JP08-281860, JP09-108621 and JP09-151203, and U.S. Patent Publication NO. 2002/0090507 disclose the methods of forming an organic solvent dispersion sol of an ATO water dispersion sol and an organic ATO (i.e., enhancing co-usability  
5 to an organic solvent by converting a hydrophilic surface of an ATO into a hydrophobic surface) and of forming heat-ray cutoff coating films respective to a hydrolic binder and an organic resin binder. However, the water ATO sol is insufficient in co-usability with an organic resin binder, and the organic ATO sol is insufficient in co-usability with a hydrolic resin binder. Further, the organic  
10 ATO sol needs a secondary process to change the hydrophilic surface into the hydrophobic surface, which causes an increase of the product cost.

Therefore, it is desired to develop an improved coating film having excellent property for cutting off heat rays.

## 15 Disclosure of Invention

An object of the present invention is directed to provide a heat-ray cutoff compound having a high transmission rate and an improved property of cutting off heat rays and a method of forming the same by means of conductive nanoparticles that is effective in cutting off heat rays.

20 Another object of the present invention is to provide a method of forming a coating film and formative substance by means of depositions or general forming techniques with conductive nanoparticles, that is effective in screening heat rays, and the coating film and formative substance manufacture by the method, in low cost.

25 In order to accomplish the above objects of the present invention, the

present invention is characterized in providing a heat-ray cutoff compound, i.e., a dispersion sol, which is formed by dispersing conductive nanoparticles in an amphoteric solvent in high concentration without an additional step for manufacturing powder to turn the nanoparticles into a hydrophobic condition, being good for commercial co-usability. The dispersion sol produced as such is efficient to manufacturing a heat-ray cutoff film and a formative object in low cost with excellent stability and co-usability to hydrolic or alcoholic resin binders and anti-hydrolic resin binders.

According to the present invention, it overcomes a problem of co-usability to hydrolic or alcoholic resin binders and anti-hydrolic resin binders by dispersing hydrophobic-surfaced conductive nanoparticles in an amphoteric solvent, capable of resulting in the form of a coating film, a film, or other formative objects, enhancing visible light transmittance, heat-ray cutoff property, endurance of wearing and weathering, low cost as well.

A compound advanced by the present invention is good for preservation stability, and provides high visible light transmittance rate and heat-ray cutoff property when it is hardened after being deposited on various films, plastic objects, or glass.

In addition, as the conductive nanoparticles such as ITO, ATO and AZO are dispersed in the amphoteric solvent, it can be easily hardened by an ultraviolet or an electronic ray even with using a hydrolic or alcoholic resin binder as well as an organic resin binder. Further, it is able to manufacture a film by way of heat or normal-temperature hardening processes.

The present invention improves the co-usability of the heat-ray cutoff film to hydrolic or alcoholic resin binders and anti-hydrolic resin binders, and provides an amphoteric solvent that enables a coating compound to be adaptable to processes of normal-temperature hardening, heat hardening, ultraviolet or

electronic ray hardening. By adding a hydrolic or alcoholic resin binder, or anti-hydrolic resin binder into such an amphoteric solvent dispersion sol, a heat-ray cutoff film or a formative object thereof is manufactured. A production cost is cheaper than before because it does not need a secondary process for a water dispersion sol in order to use the anti-hydrolic resin binder.

#### Brief Description of Drawings

FIG. 1 illustrates a profile of light transmission spectrum for a coating film containing an ITO, which is obtained from Example 3.

FIG. 2 illustrates a profile of light transmission spectrum for a coating film containing an ATO, which is obtained from Example 4.

FIG. 3 illustrates a profile of light transmission spectrum for a coating film containing an ATO with different ration of Sb, which is obtained from Example 4.

FIG. 4 illustrates a profile of light transmission spectrum for a cohesive film containing an ATO, which is obtained from Example 4.

FIG. 5 illustrates a microscopic view, by a scanning electron microscopy (SEM), of a heat-ray cutoff coating film containing conductive nanoparticles, which is obtained from Example 4.

#### Best Mode for Carrying out the Invention

[Manufacturing a bilaternal solvent dispersion sol]

##### 1. Conductive nanoparticles

Conductive nanoparticles of the present invention were used with nanoparticles of metal oxides having excellent conductivity, such as ATOs, ITOs, and antimony-doped zinc oxides (AZOs). The metal oxide nanoparticles have

grain diameters under 200 nm, preferably under 100nm, more preferably in the range of 10 ~ 80 nm, and the nanoparticles are dispersed into an amphoteric solvent such that particles more than 60 % have their diameters within 100 nm. Small particles under 200 nm do not induce the dispersion in the range of visible  
5 light, retaining the transparency of the coating film. For the compound in use of forming a coating film to screen heat rays, by the present invention, conductive nanoparticles, such as ATO, ITO, AZO, and so on, were used with varying a fine component ratio of powder in accordance with necessity. The conductive nanoparticles are manufactured by means of a general method,  
10 accompanying with a product made by PMT Co., Keeling & Walker Co., Nano Korea Co., and so on, or a compound power having an appropriate fine component ratio.

While there is no limit to the amount of the conductive nanoparticles used in the dispersion of the amphoteric solvent, it is exhorted to be established  
15 in the range of 1 ~ 80 wt%, preferably in the range of 20 ~ 60 wt%.

## 2. Amphoteric solvent

It is generally frequent for a solvent to be used in dispersion of the conductive nanoparticles to employ a polarized organic solvent such as water or  
20 alcohol, or a non-polarized organic solvent such as toluene or xylene. If a solvent of a dispersion sol manufactured by the above condition is a polarized solvent like water or alcohol, it is unable to be adoptable to anti-hydrolic resin binder. To the contrary, if a solvent of a dispersion sol is a non-polarized organic solvent, it is unable to be adoptable to hydrolic resin binder. Therefore,  
25 there has been a limit in application because it was impossible to use a single dispersion sol for a variety of resin binders. Further, as a powder surface in the conductive nanoparticles shows its hydrophilic property, it needs a process for



manufacturing an additional powder to convert the powder surface into a hydrophobic property for the dispersion of non-polarized organic solvent, which raises a time and cost for that.

Therefore, the present invention makes it enable to be used by mixing  
5 the nanoparticles with all kinds of resin binders without processing such a secondary treatment for converting the powder surface of the conductive nanoparticles into a hydrophobic property, by manufacturing a dispersion sol from using the amphoteric solvent. There are many kinds to be usable as the amphoteric solvent adoptable to the dispersion of the conductive nanoparticles,  
10 such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, so on, but other kinds of the amphoteric solvents may be also available without limitation on the above composites. While there is no limit to the amount of the solvent used in the dispersion of the amphoteric solvent, it is exhorted to be established  
15 in the range of 20 ~ 99 wt%, preferably in the range of 50 ~ 80 wt%.

### 3. Additive

When the conductive nanoparticles are dispersed in the amphoteric solvent, it is available to add several additives, such as a surface charge  
20 mediating agent and a dispersing agent, in order to enhance the efficiency of the surface property and dispersion of the dispersion sol formed therein.

(1) Surface charge mediating agent: Dispersion by electrostatic repulsion.

The conductive nanoparticles have charges on their surfaces in the dispersion sol. The surface charge mediating agent can make the surface  
25 charges be stronger and all the nanoparticles have the same charges. Counter-ions surround the surface charges of the nanoparticles to form electrical double layers. As the double layers are thicker, the dispersion sol becomes more

stable.

While an isoelectric point of the surface in the conductive nanoparticles used in the present invention is variable in accordance with kinds and states of the nanoparticles, ATO has  $\text{pH}_{\text{Ipe}} = 3.7$  and ITO has  $\text{pH}_{\text{Ipe}} = 8.5$ . Thus, a  
5 suspension is stabilized in the conditions of  $\text{pH} > 8$  in ATO, while of  $\text{pH} < 6$  in ITO. The amount and kind of the surface charge mediating agent are preferred to be set in concordance with a dispersion condition because they are variable in accordance with the composition, the kinds and the additive amount of the nanoparticles. When an hydrochloric acid is used as a surface charge  
10 mediation agent for an ATO containing antimony of 10 wt%, it is available to use an acid of  $5 \times 10^{-4} - 3.5 \times 10^{-3}$  g per a nanoparticle of 1 g.

The ITO nanoparticles has an isoelectric point higher different from the ATO nanoparticles and the mediation on the surface charges are determined in accordance with an object and use of the dispersion sol. In manufacturing a  
15 dispersion sol with a high concentration and a low viscosity, it is preferred to process it with a dispersing agent after dispersing the particles in the amphoteric solvent without mediating the surface charges. The kinds of acids usable in the present invention are organic acids, inorganic acids, and polymeric acids. The organic acids include acetic acids or glacial acetic acids, while the inorganic  
20 acids include hydrochloric acids, nitric acids, phosphoric acids, sulfuric acids, and so on. The polymeric acids include polyacrylic acids as an example. The kinds of the acids are not limited in the above and others are available thereto.

(2) Dispersing agent: Dispersion by an effect of steric hindrance.

A dispersing agent effective in the steric hindrance has two distinctive  
25 structures as follows.

a. The dispersing agent is able to be absorbingly adhesive to the surfaces of the conductive nanoparticles, retaining strong adhesion

to a surface of a pigment because it has one or more functional radicals having affinities for the conductive nanoparticles.

- b. With hydrocarbon entities good for co-usability, after being absorbed on the conductive nanoparticles, the hydrocarbon entities dangle from the amphoteric solvent around the conductive nanoparticles. Such a state, where the hydrocarbon entities are hanging down from the amphoteric solvent and absorbed on the surfaces of the conductive nanoparticles, is called steric hindrance or entropic stabilization.

Interactions between polymeric portions of the dispersion agent and the amphoteric solvent make envelopes around the conductive nanoparticles thicker, enforcing the stability thereof. Such stabilization enables the dispersion sol to be adaptable to all the hydrolic resin binders partially using the anti-hydrolic resin binders and solvents. The dispersing agent is assistant to a procedure of dispersing the conductive nanoparticles into the amphoteric solvent, or is assistant to a procedure of dispersing the conductive nanoparticles into the amphoteric solvent together with the surface charge mediating agent. Accordingly, the dispersion agent is effective in reducing the viscosity, preventing re-cohesion of the nanoparticles, by maintaining distances between the nanoparticles due to the electrostatic repulsion or the steric hindrance arising from the absorption to the dispersion sol dispersed into the amphoteric solvent.

The dispersing agent is classified into one having an amin radical and the other having an acid radical. In detail, it is available to use anti-terra-203, anti-terra-204, anti-terra-205, anti-terra-206, anti-terra-U, anti-terra-U100, anti-terra-U80, BYK-154, BYK-220S, BYK-P104, BYK-P104S, BYK-P105, BYK-9075, BYK-9076, BYK-9077, Byklumen, Disperbyk, Disperbyk-101, Disperbyk-

102, Disperbyk-103, Disperbyk-106, Disperbyk-107, Disperbyk-108, Disperbyk-110, Disperbyk-111, Disperbyk-112, Disperbyk-115, Disperbyk-116, Disperbyk-130, Disperbyk-140, Disperbyk-142, Disperbyk-160, Disperbyk-161, Disperbyk-162, Disperbyk-163, Disperbyk-164, Disperbyk-166, Disperbyk-167, Disperbyk-169, Disperbyk-170, Disperbyk-171, Disperbyk-174, Disperbyk-176, Disperbyk-180, Disperbyk-181, Disperbyk-182, Disperbyk-183, Disperbyk-184, Disperbyk-185, Disperbyk-187, Disperbyk-190, Disperbyk-191, Disperbyk-192, Disperbyk-2000, Disperbyk-2001, Disperbyk-2050, Disperbyk-2070, Disperbyk-2150, Lactimon, Lactimon-WS, and so on (BYK Chemie GmbH).

10       The coating film using the amphoteric solvent dispersion sol manufactured by the method of the present invention is a high surface resistance over  $1 \times 10^6 \Omega \cdot \text{cm}$ , which is advantageous to be adoptable to audio systems of various communication apparatuses and in automobiles because it is capable of transmitting radio frequencies emitted from mobile phones, televisions, or  
15       radios. The amount used in the dispersing agent is 1 ~ 30 wt% in weight ratio to the conductive nanoparticles.

#### 4. Photopolymerization initiator

20       It is available to add a photopolymerization initiator for the purpose of easily hardening the dispersion sol of the present invention when it is exposed to chemical rays (ultraviolet, infrared). Such photopolymerization initiators include 1-hydroxy-cyclo-hexyl-phenyl-ketone, benzyl-dimethyl-ketal, hydroxyl-dimethyl-aceto-phenone, benzoin, benzoin-methyl-ether, benzoin-isopropyl-ether, benzoin-butyl-ether, benzyl, benzophenone, 2-hydroxy-2-methylpropiophenone,  
25       2,2-dietoxy-ethophenone, anthraquinone, chloroanthraquinone, etylantraquinone, butylantraquinone, 2-chlorothyoksantone, alpha-chlorometylnaphthalene, and anthracene. In detail, there are Lucirin (BASF Co.), Darocur MBF, Igacure-184,

Igacure-651, Igacure-819, Igacure-2005 (Ciba Geigy Co.), and so on. It is possible to combine more one agents among the photopolymerization initiators proposed above. A ratio of the photopolymerization initiators is preferred to be 0.1 ~ 10 wt% to 100 wt% of the dispersion sol, prederably 1 ~ 5 wt%.

5

[Heat-ray cutoff coating film]

### 1. Resin binder

Although without a specific limitation in the kinds of the resin binders composing compounds of the coating films, it is preferable to use one capable of forming a coating film with excellent transparency, and possible to select one or more two kinds in accordance with the condition of hardening such as ultraviolet hardening when there is co-usability between the resin binders. The hydrolic resin binders include water-soluble alkyd, polyvinylalcohol and polybutylalcohol, and hydrolic emulsion-type resin binders include acrylyl, acrylylstyrene, and super-acid vinyl. Alcoholic resin binders include polyvinylbutyral and polyvinylacetal. Anti-hydrolic heat-hardening resin binders include acrylyl, polycarbonate, polychloride vinyl, urethane, melamine, alkyd, polyester, and epoxy, while ultraviolet-hardening resin binders include epoxy acrylylate, polyether acrylylate, polyester acrylylate, and urethane-  
20 metamorphosed acrylylate.

The amount used in the resin binder is 1 ~ 95 wt% for 100 wt% of a coating compound, prederably about 5 ~ 40 wt%.

### 2. Manufacturing heat-ray cutoff coating solution

25 It is able to easily produce a heat-ray cutoff coating compound with superior properties in visible right transmission and heat-ray cutoff in low cost by mixing the resin binder with a sol obtained by dispersing the conductive

nanoparticles in the amphoteric solvent.

It is permissible to set a compounding ratio of the conductive nanoparticles dispersion sol and the resin binder from 97:3 to 30:70 in weight ratio, preferably 95:5 through 70:30.

5

[Property of heat-ray cutoff coating film]

There are a variety of ways to coating a compound characterized in screening heat rays, such as spinal coating, deep coating, roll coating, bar coating, screen printing, photogravure, microgravure, offset, and so on.

10

A heat-ray cutoff coating film produced by the present invention has a structure that the conductive nanoparticles are uniformly distributed in a hydrolic or alcoholic, or anti-hydrolic resin binder. Such a heat-ray cutoff coating film displays its function of screening heat rays higher along much conductive nanoparticles used therein under the same conditions with the kinds of apparatus, conductive nanoparticles and additive. With the same amount of the conductive nanoparticles and the same amount of the additive, it is inclined to make an effect of screening heat rays higher as the conductance of the conductive nanoparticles, i.e., specific resistance is lower. For example, ATO nanoparticles, which has conductance variable dependent on an engagement ratio of antimony therein, is preferred to have its specific resistance under 10  $\Omega \cdot \text{cm}$ , preferably under 3.0  $\Omega \cdot \text{cm}$ . Here, the best feature of screening heat rays appears from an ATO containing antimony of 10 wt% that corresponds to the lowest specific resistance.

15

20

25

However, it is also inclined to cause a visible light transmission rate to be increased in accordance with an increase of the amount of antimony. Along the increase of antimony, a color of the ATO nanoparticles powder goes to pale blue-gray from blue-gray, from which a color of a coating film changes to

yellowish green from blue. These changes of colors causes an absorption peak value to vary around a wavelength of 550 nm, which makes it predictable to change the visible light transmission rate. The absorption for a visible light is higher in a blue series while lower in a yellow series.

5

[Evaluation for heat-ray cutoff coating film]

The coating film produced by the present invention was evaluated by means of the methods as follows.

#### 10 1. Optical characteristic

A transmittance was carried out for light in the range of 200 nm through 2500 nm by means of UV/VIS/NIR Spectrometer (CARY 5G, Varian Co.).

##### (1) Visible light transmittance (VLT):

The visible light transmittance was represented in a value obtained by  
15 calculating a ratio of a transmitted pencil to an incident pencil of sunlight on the standard of ASTM E903-82 (JIS R 3106, KS L2514), after measuring spectrum transmittance at 41 wavelength points every 10 nm in the range from 380 nm to 780 nm by means of a spectrum photometer. The sunlight means a distribution of relative spectro-illumination in the scope of mixed direct and scattered light,  
20 as composite sunlight for designing illumination offered by International Commission on Illumination (CIE). The pencil means a wavelength integral with a product of spectro-emission flux and spectro-luminous efficiency.

##### (2) IR cutoff

The IR cutoff represents an area ratio excepting an integral value of a  
25 transmitted area over the overall size after measuring a transmittance in the range of wavelength 800 ~ 1800 nm by means of a spectrum photometer.

## 2. Endurance against wearing (measuring surface hardening)

Pencil hardening intensity was measured on the standard of JIS K5651-1966

## 5 3. Adhesion property

A laminate test was performed with a cross-cut cellotape for a hardened coating film.

In detail, a cellotape attaches and strip off three times from the coating film in which cutout lines reaching a substrate are inserted in the pitch of 1 mm  
10 with hundred scales of 1 mm<sup>2</sup>, the cutout lines being arranged crosswise and lengthwise in number of 11.

○: No lamination of a crosslinked hardened coating film.

△: The case that the number of lamination scales is 1 ~ 50.

×: The case that the number of lamination scales is 51 ~ 100.

15

## 4. Surface smoothness

Monitoring flatness of the coating film, after being hardened, by means of vision or an electro-microscopy was carried out.

○: Excellent as like a mirror face

20 △: Some disordered on the surface

×: So many wrinkles on the surface

## 5. Weatherability

It represented that "○" corresponds to when visible light and sunlight  
25 transmittance retain over 80 % of their initial values contemporaneously, after illuminating for 2000 hours in a carbon arc sunshine weathermeter, while "×" corresponds when under 80 % of their initial values.



## 6. Preservation stability

It represented deterioration along a lapse of time in accordance with variations of phase separation, cohesion, and an increase of viscosity.

### 5 [Manufacturing dispersion sol of conductive nanoparticles]

#### [Example 1]

After mixing ITO nanoparticles (Nano Korea Co.) of 40 ~ 80g with an amphoteric solvent of 120 ~ 160g, zirconia balls were charged up to 50 vol% and then dispersed in the mixed solution for 24 hours. And, disperbyk-180  
10 (BYK Chemie Co.), as a dispersing agent, of 2 ~ 10g was added thereto and uniformly mixed therewith by an agitator, so that a high performance ITO nanoparticles dispersion sol was obtained with good co-usability to hydrolic or alcoholic, or anti-hydrolic resin binders. In the case of mixing the ITO nanoparticles with an ultraviolet hardening resin binder, a photo-initiator  
15 Irgacure184 (Ciba Geigy Co.) of 1 ~ 5g was added thereto to obtain the dispersion sol.

#### [Comparison 1]

A dispersion sol was obtained from the same processing conditions but a  
20 solvent for dispersion was an alcohol (methanol, ethanol).

#### [Example 2]

After mixing HCl of  $5 \times 10^{-4} \sim 3.5 \times 10^{-3}$  g, for adjusting pH concentration, with a solution composed of ATO nanoparticles (Keeling & Walker Co.), which  
25 contain antimony of 5, 10, 15 and 20% in weight ratio, and an amphoteric solvent of 120 ~ 160g, zirconia balls were charged up to 50 vol% and then dispersed in the mixed solution for 24 hours to control surface charges of the

nanoparticles. And, Anti-Terra-U100 (BYK Chemie Co.), as a dispersing agent, of 2 ~ 10g was added thereto and uniformly mixed therewith by an agitator, so that a high performance ATO nanoparticles dispersion sol was obtained with good co-usability to hydrolic or alcoholic, or anti-hydrolic resin binders. In the case of mixing the ATO nanoparticles with an ultraviolet hardening resin binder, a photo-initiator Irgacure184 (Ciba Geigy Co.) of 1 ~ 5g was added thereto to obtain the dispersion sol.

#### [Comparison 2]

A dispersion sol was obtained from the same processing conditions but a solvent for dispersion was an organic solvent (toluene, benzene).

#### [Manufacturing coating compound]

#### [Example 3]

A ultraviolet hardening heat-ray cutoff coating solution was obtained by uniformly mixing the ITO nanoparticles dispersion sol with a hardening deposition film, which had been made from an ultraviolet hardening resin (solid powder 100%, SK-UCB Co.) of acrylate series, in an agitator, after adjusting a volume ratio on conductive nanoparticles : binder = 5:95 ~ 80:20.

A heat-ray cutoff film was obtained from that after coating a heat-ray cutoff coating compound on a polycarbonate substrate with thickness of 125  $\mu\text{m}$  in powder thickness of 0.5 ~ 5  $\mu\text{m}$  by means of Meyer Rod #6 ~ 10, the solvent was evaporated by hot air and then the coating film was hardened by being irradiated with a high-pressure mercury lamp of 100W in a conveying velocity of 20 m/min.

The following Table 1 arranges resulting data evaluated by the aforementioned test methods for various ITO heat-ray cutoff films manufactured

by the above processes.

[Table 1 : ITO heat-ray cutoff films]

Sample No.	ITO (Vol%)	Resin Binder (Vol%)	Disp. Sol.	Meyer Rod #	VLT	IR-C	Adhesion	Pencil Intensity	Sub.	Pres. stability
1	3.32	37.00	EGPE	10	83.4	70.5	0	2H↑	PC	0
2	3.92	27.27	EGBE	10	82.1	75.1	0	2H↑	PC	0
3	4.20	22.73	EGEE	10	82.3	75.9	0	2H↑	PC	0
4	4.48	18.18	EGPE	10	81.8	77.6	0	2H↑	PC	0
5	4.64	15.45	EGME	10	82.4	77.0	0	2H↑	PC	0
6	4.79	13.06	EGEE	10	76.9	83.1	0	2H↑	PC	0
7	4.97	10.23	EGPE	10	77.5	81.1	0	2H↑	PC	0
8	5.04	9.09	EGBE	10	77.7	80.9	0	2H↑	PC	0
Comp.1	1.81	61.55	MeOH	10	86.0	59.2	-	-	PC	×
Comp.1	4.64	15.45	EtOH	10	82.4	77.0	-	-	PC	×

\* EGME: ethylene glycol monomethyl ether, EGEE: ethylene glycol monoethyl ether, EGPE: ethylene glycol monopropyl ether, EGBE: ethylene glycol monobuthyl ether, MeOH: methyl alcohol, EtOH: ethyl alcohol.

As can be seen from Table 1, the heat-ray cutoff films (the samples 1 ~ 8) has the preservation stabilities better than those of other heat-ray cutoff films (the comparisons 1 and 2), but similar in the visible light transmittance (VLT) and the heat cutoff rate (IR-C).

FIG. 1 depicts profiles of light transmission spectrums of the coating films for the samples #1, 3 and 6 shown in Table 1. As illustrated, they show high performance of screening infrared rays and visible light transmission.

## [Example 4]

A ultraviolet hardening heat-ray cutoff coating solution was obtained by uniformly mixing the ATO nanoparticles dispersion sol of Example 2 with a hardening deposition film, which had been made from an ultraviolet hardening resin (solid powder 100%, SK-UCB Co.) of acrylate series, in an agitator, after  
 5 adjusting a volume ratio on conductive nanoparticles : binder = 15:85 ~ 80:20.

## 1) Coating Meyer Rod

A heat-ray cutoff film was obtained from that after coating a heat-ray  
 10 cutoff coating compound on a polyethyleneterephthalate (PET) substrate with thickness of 25  $\mu\text{m}$  or a polycarbonate substrate with thickness of 125  $\mu\text{m}$  in powder thickness of 0.5 ~ 5  $\mu\text{m}$  by means of Meyer Rod #6 ~ 10, the solvent was evaporated by hot air and then the coating film was hardened by being irradiated with a high-pressure mercury lamp of 100W in a conveying velocity of 20 m/min.  
 15 The following Table 2 arranges resulting data evaluated by the aforementioned test methods for ATO heat-ray cutoff films manufactured by the above processes.

[Table 2: ATO heat-ray cutoff films]

Sam. No.	ITO Vol%	Resin Binder Vol%	Sol.	Acid	Meyer Rod #	VLT	IR-C	Adh esio n	Pencil Intensi ty	Sub.	Preserv. stability
9	3.30	13.15	EGEE	HCL	10	77.5	71.5	0	2H↑	PET	0
10	3.41	10.25	EGPE	AcOH	10	75.7	72.59	0	2H↑	PET	0
11	3.50	8.17	EGBE	HNO <sub>3</sub>	10	73.8	74.04	0	2H↑	PET	0
12	3.69	3.70	EGBE	H <sub>3</sub> (PO <sub>4</sub> )	10	69.2	72.98	0	2H↑	PET	0
13	3.74	2.49	EGPE	HCL	10	72.8	74.30	0	2H↑	PET	0

14	3.78	1.65	EGBE	HCL	10	73.4	72.79	0	2H↑	PET	0
15	3.81	0.92	EGME	HCL	10	74.3	74.47	0	2H↑	PET	0
16	4.31	9.09	EGME	HCL	7	73.5	71.3	0	2H↑	PET	0
17					8	73.9	71.5	0	2H↑	PET	0
18	4.47	15.45	EGEE	HCL	7	71.7	73.8	0	2H↑	PET	0
19					8	71.8	73.7	0	2H↑	PET	0
20	4.57	13.64	EGBE	HCL	7	72.3	74.0	0	2H↑	PET	0
21					8	71.2	74.3	0	2H↑	PET	0
22	4.68	11.82	EGPE	HCL	7	71.2	75.7	0	2H↑	PET	0
23					8	69.5	77.5	0	2H↑	PET	0
24	4.74	10.91	EGEE	HCL	7	71.6	73.8	0	2H↑	PET	0
25					8	70.6	75.2	0	2H↑	PET	0
26	4.79	10.00	EGME	HCL	7	72.1	73.0	0	2H↑	PET	0
27					8	69.9	78.3	0	2H↑	PET	0
28	4.85	9.09	EGEE	HCL	7	70.0	75.9	0	2H↑	PET	0
29					8	70.3	78.2	0	2H↑	PET	0
30	5.54	9.09	EGME	HCL	10	67.6	82.0	0	2H↑	PET	0
31					8	70.9	75.8	0	2H↑	PET	0
32	6.92	9.09	EGME	HCL	8	65.7	81.9	0	2H↑	PET	0
Comp.3	4.43	-	toluene	HCL	-	-	-	-	-	-	-
Comp.4	4.79	-	xylene	HCL	-	-	-	-	-	-	-
Comp.5	5.54	-	bensen e	HCL	-	-	-	-	-	-	-

\* EGME: ethylene glycol monomethyl ether, EGEE: ethylene glycol monoethyl ether, EGPE: ethylene glycol monopropyl ether, EGBE: ethylene glycol

monobuthyl ether

As can be seen from Table 2, the properties of the heat-ray cutoff films (the samples #9~32), which were formed by dispersing the conductive nanoparticles in the amphoteric solvent or the hydrochloric acid, are similar to those of the samples #1~8 shown in Table 1. In other words, while the former examples used solvents different in polarity, the present invention was able to obtain the similar results even with a resin binder belonging to the same series, i.e., an ultraviolet hardening resin. By the contrary, in the cases of the comparisons 3~5, the non-polarized organic solvent, like toluene, xylene, and benzene, and the hydrochloric acid did not effective in dispersing the ATO as the conductive nanoparticles. In order to conduct dispersion to a non-polarized organic solvent, it needs an additional process for manufacturing powder to change surfaces of the ATO nanoparticles into hydrophobic property.

FIG. 2 shows profiles of light transmission spectrums of the coating films for the samples #9, 15 and 32 shown in Table 2. As illustrated, they show high performance of screening infrared rays and visible light transmission.

The following Table 2 arranges resulting data evaluated by the aforementioned test methods for ATO heat-ray cutoff films in accordance with the content of antimony.

[Table 3; ATO film properties according to antimony (Sb) content]

Sample No.	Sb (Vol%)	ATO (Vol%)	Resin Binder (Vol%)	Meyer Rod #	VLT	IR-C	Adhesion	Pencil Intensity	Sub.	Pres. stability
33	5	4.58	13.64	8	75.8	67.6	0	2H↑	PET	0
34		4.85	9.09	8	73.0	71.6	0	2H↑	PET	0
35	10	4.58	13.64	7	72.3	74.0	0	2H↑	PET	0
36				8	71.2	74.3	0	2H↑	PET	0
37		4.85	9.09	7	70.0	75.9	0	2H↑	PET	0
38				8	70.3	78.2	0	2H↑	PET	0
39	15	4.58	13.64	7	76.1	67.3	0	2H↑	PET	0
40				8	75.8	66.4	0	2H↑	PET	0
41		4.85	9.09	7	76.1	68.1	0	2H↑	PET	0
42				8	77.0	68.8	0	2H↑	PET	0
43				10	70.9	76.4	0	2H↑	PET	0
44	20	4.58	13.64	8	78.0	64.6	0	2H↑	PET	0
45		4.85	9.09	8	76.4	63.1	0	2H↑	PET	0

FIG. 3 shows profiles of light transmission spectrums of the coating films for the samples #34, 38, 42 and 45 shown in Table 3. As illustrated, they show high performance of screening infrared rays and visible light transmission.

5

## 2) Microgravure coating

A heat-ray cutoff film was obtained from that after coating a heat-ray cutoff coating compound in powder thickness of 1.7 ~ 3.0  $\mu\text{m}$  by means of microgravure head #6H ~ 9H, the solvent was evaporated by hot air for 30 seconds and then the coating film was hardened by being irradiated with a high-

10

pressure mercury lamp, which can be powered up to 1000 mJ/cm, in a conveying velocity of 20 m/min. The following Table 4 arranges resulting data evaluated by the aforementioned test methods for the heat-ray cutoff films manufactured by the above processes.

5

[Table 4: Microgravure coated heat-ray cutoff films]

Sample No.	ATO (Vol%)	Resin Binder (Vol%)	Conveying velocity	Cell #	VLT	IR-C	Adhesion	Pencil Intensity	Sub.	Pres. stability
46	4.43	9.09	40 m/min	6H	75.1	71.8	0	2H↑	PET	0
47				9H	70.4	78.9	0	2H↑	PET	0

FIG. 4 shows profiles of light transmission spectrums of the coating films for the samples #46 and 47 shown in Table 4. As illustrated, they show high performance of screening infrared rays and visible light transmission.

10

FIG. 5 is a photograph by a scanning electron microscopy, obtained from the results of Example 4, showing heat-ray cutoff films with thickness of 3.10  $\mu\text{m}$  through 3.15  $\mu\text{m}$ .

## [Example 5]

15

A heat hardening heat-ray cutoff coating solution was obtained by uniformly mixing the ATO nanoparticles dispersion sol of Example 3 with a hardening deposition film, which had been made from an a heat hardening resin of acrylylate series, in an agitator, after adjusting a volume ratio on ATO : binder = 15:85 ~ 80:20.

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## [Example 6]

A normal-temperature hardening heat-ray cutoff coating solution was



obtained by uniformly mixing the ATO nanoparticles dispersion sol of Example 3 with a normal-temperature hardening resin binder, which had been made by solving a polyvinylalcohol into distilled water or an alcohol, in an agitator

## 5 Industrial Applicability

The heat-ray cutoff films according to the present invention are effective in screening heat is advantageous to be associated with means for preventing malfunctions of integrated circuits or electronic components, or for reducing the costs for cooling and heating by lessening the amount of solar energy going in  
10 and out of rooms and automobiles through windows. In addition, it is possible to offer effects of cutoff infrared rays when they are applied to various products such as optical fibers, sun visors, PET vessels, packaging films, glasses, textile goods, peep holes of heaters, heating apparatuses, and so on.

The heat-ray cutoff films according to the present invention are  
15 advantageous to retaining the freshness of drinking waters, especially during the summer season, because they protect infrared rays when they attaches to vessels containing the drinking waters.

Furthermore, the heat-ray cutoff films according to the present invention provides effects of retarding the temperature falling of beverages or foods,  
20 because they protect infrared rays when they attaches to vessels containing the beverages or the foods.

## WHAT IS CLAIMED IS:

1. A compound for producing a heat-ray cutoff film, which comprises conductive nanoparticles uniformly dispersed in an amphoteric solvent.

5

2. The compound according to claim 1, wherein the conductive nanoparticles include ATO, ITO, and AZO.

3. The compound according to one of claims 1 and 2, wherein the  
10 conductive nanoparticle is sized in diameter under 200 nm and in the range of 1 ~ 80 wt%, while the amphoteric solvent has 20 ~ 99 wt%.

4. The compound according to claim 3, wherein the amphoteric  
15 solvent includes ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, or ethylene glycol monobutyl ether.

5. The compound according to claim 1, which further comprises an acid for adjusting surface charges of the conductive nanoparticles, the acid including an organic acid, an inorganic acid, or polymeric acid.

20

6. The compound according to claim 5, wherein the conductive nanoparticle is an ATO nanoparticle containing Sb with 5 ~ 20 wt% and the acid is included with the range of  $5 \times 10^{-4} \sim 3.5 \times 10^{-3}$  g to the conductive nanoparticle.

25 7. The compound according to one of claims 1 through 5, which further comprises a dispersing agent for stabilizing the conductive nanoparticles.

8. The compound according to claim 7, wherein the dispersing

agent is included with 1 ~ 30 wt% to the conductive nanoparticle, while the dispersing agent includes a dispersing agent containing an amin radical, a dispersing agent containing an acid radical, or a neutral dispersing agent.

5           9.       The compound according to claim 7, which further comprises more one resin binder among an anti-hydrolic resin binder and a hydrolic or alcoholic resin binder.

10           10.       The compound according to claim 9, wherein the resin binder is in the range of 1 ~ 95 wt%.

15           11.       The compound according to claim 10, wherein the hydrolic resin binder includes a water-soluble alkyd, a polyvinylalcohol, a polybutylalcohol, an acrylic, an acrylylstylene, or a super-acid vinyl, the alcoholic resin binder includes a polyvinylbutyral or a polyvinylacetal, and the anti-hydrolic resin binder includes a heat-hardening resin binder including an acrylic, a polycarbonate, a polychloride vinyl, an urethane, a melamine, an alkyd, a polyester, or an epoxy, or an ultraviolet-hardening resin binder including an epoxy acrylylate, a polyether acrylyate, a polyester acrylylate, or an urethane-  
20 metamorphosed acrylylate.

          12.       The compound according to claim 9, wherein the conductive nanoparticle is sized in diameter under 200 nm and in the range of 1 ~ 80 wt%, while the amphoteric solvent has 20 ~ 99 wt%.

25

          13.       The compound according to claim 12, wherein the amphoteric solvent includes ethylene glycol monomethyl ether, ethylene glycol monoethyl

ether, ethylene glycol monopropyl ether, or ethylene glycol monobutyl ether.

14. The compound according to claim 12, wherein the conductive nanoparticle is an ATO nanoparticle containing Sb with 5 ~ 20 wt% and the acid  
5 is included with the range of  $5 \times 10^{-4} \sim 3.5 \times 10^{-3}$  g to the conductive nanoparticle.

15. The compound according to claim 12, wherein the dispersing agent is included with 1 ~ 30 wt% to the conductive nanoparticle, while the dispersing agent includes a dispersing agent containing an amin radical, a  
10 dispersing agent containing an acid radical, or a neutral dispersing agent.

16. A method of forming a compound for producing a heat-ray cutoff film, which comprises uniformly dispersing conductive nanoparticles uniformly in an amphoteric solvent.

15

17. The method according to claim 16, wherein the conductive nanoparticle is sized in diameter under 200 nm and in the range of 1 ~ 80 wt%, while the amphoteric solvent has 20 ~ 99 wt%.

20

18. The method according to one of claims 16 and 17, wherein the conductive nanoparticles are dispersed in the amphoteric solvent by means of a dispersing agent and at least more one among acids to adjust surface charges of the conductive nanoparticles.

25

19. The method according to claim 18, wherein the conductive nanoparticle is an ATO nanoparticle containing Sb with 5 ~ 20 wt%, the acid is included with the range of  $5 \times 10^{-4} \sim 3.5 \times 10^{-3}$  g to the conductive nanoparticle,

the dispersing agent is included with 1 ~ 30 wt% to the conductive nanoparticle, and the dispersing agent includes a dispersing agent containing an amin radical, a dispersing agent containing an acid radical, or a neutral dispersing agent.

5           20.     A method of forming a heat-ray cutoff film, comprising the steps of:

              mixing the compound defined in claim 19 with one more resin binders among a anti-hydrolic resin binder and a hydrolic or alcoholic resin binder; and

              depositing the mixed composite on a substrate and hardening the  
10     deposited composite by a chemical ray using an ultraviolet or an electronic ray, or by heat.

              21.     The method according to claim 20, wherein the resin binder has  
15     1 ~ 95 wt%.

              22.     The method according to claim 20, wherein the substrate is an  
alternative one of a glass, a ceramic, a plastic, a metal, and a product of the  
formers, and the compound including the resin binder is processed in a plastic  
condition under 50 ~ 500 °C.

20           23.     The method according to claim 20, wherein the substrate is a polycarbonate-series resin, a poly (metha) acrylylesther-series resin, a saturated fatty acid, or a cyclo-olefin resin, and hardened by an ultraviolet.

25           24.     The method according to claim 23, wherein the ultraviolet is irradiated in the range of 500 ~ 1500 mJ/cm and the hardening proceeds in the velocity of 15 ~ 50 m/min.

25. A heat-ray cutoff film manufactured by the method as defined in claim 18.

5 26. A heat-ray cutoff film manufactured by the methods as defined claims 19 through 24.

27. The heat-ray cutoff film according to claim 26, wherein the film has a surface resistance of  $106 \Omega/\square$ .

10 28. The heat-ray cutoff film according to claim 26, wherein the film has thickness under  $5 \mu\text{m}$ , pencil intensity above 1H, visible light transmittance above 50%, and heat-ray cutoff rate of 50%.

15 29. A method of screening heat rays by attaching the heat-ray cutoff film on a vessel containing drinking water, preventing the heat rays from going in and out of the vessel to retain temperature of the drinking water.

20 30. A method of screening heat rays with a heat-ray cutoff film, comprising the steps of:

forming a compound by uniformly dispersing conductive nanoparticles in an amphoteric solvent;

mixing the compound with one more resin binders among a anti-hydrolic resin binder and a hydrolic or alcoholic resin binder;

25 depositing the mixed composite of the compound and resin binder on a substrate and then forming the heat-ray cutoff film by hardening the deposited composite by a chemical ray using an ultraviolet or an electronic ray, or by heat;

and

coating the heat-ray cutoff film on a surface of a vessel containing a content.

5           31.     The method according to claim 30, wherein the conductive nanoparticle is sized in diameter under 200 nm and in the range of 1 ~ 80 wt%, while the amphoteric solvent has 20 ~ 99 wt%.

          32.     The method according to one of claims 30 and 31, wherein the  
10   conductive nanoparticles are dispersed in the amphoteric solvent by means of a dispersing agent and at least more one among acids to adjust surface charges of the conductive nanoparticles.

          33.     The method according to claim 32, wherein the conductive  
15   nanoparticle is an ATO nanoparticle containing Sb with 5 ~ 20 wt%, the acid is included with the range of  $5 \times 10^{-4} \sim 3.5 \times 10^{-3}$  g to the conductive nanoparticle, the dispersing agent is included with 1 ~ 30 wt% to the conductive nanoparticle, and the dispersing agent includes a dispersing agent containing an amin radical, a dispersing agent containing an acid radical, or a neutral dispersing agent.

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          34.     The method according to claim 30, wherein the resin binder has 1 ~ 95 wt%.

          35.     The method according to claim 30, wherein the substrate is a  
25   polycarbonate-series resin, a poly (metha) acrylylesther-series resin, a saturated fatty acid, or a cyclo-olefin resin, and hardened by an ultraviolet.

36. The method according to claim 30, wherein the vessel is made of a metal, a ceramic, or a plastic, containing drinking waters or foods.



Fig. 1

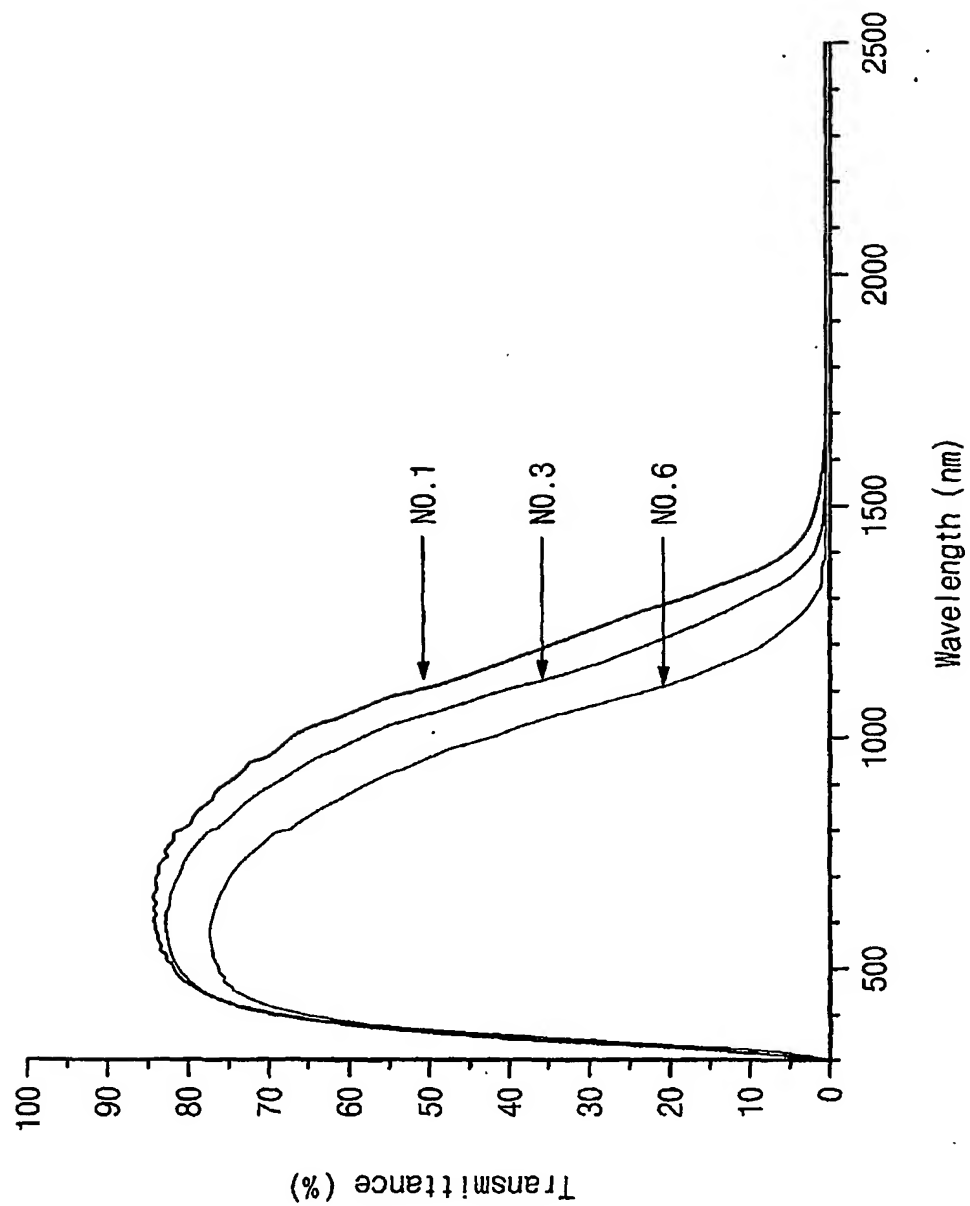


Fig. 2

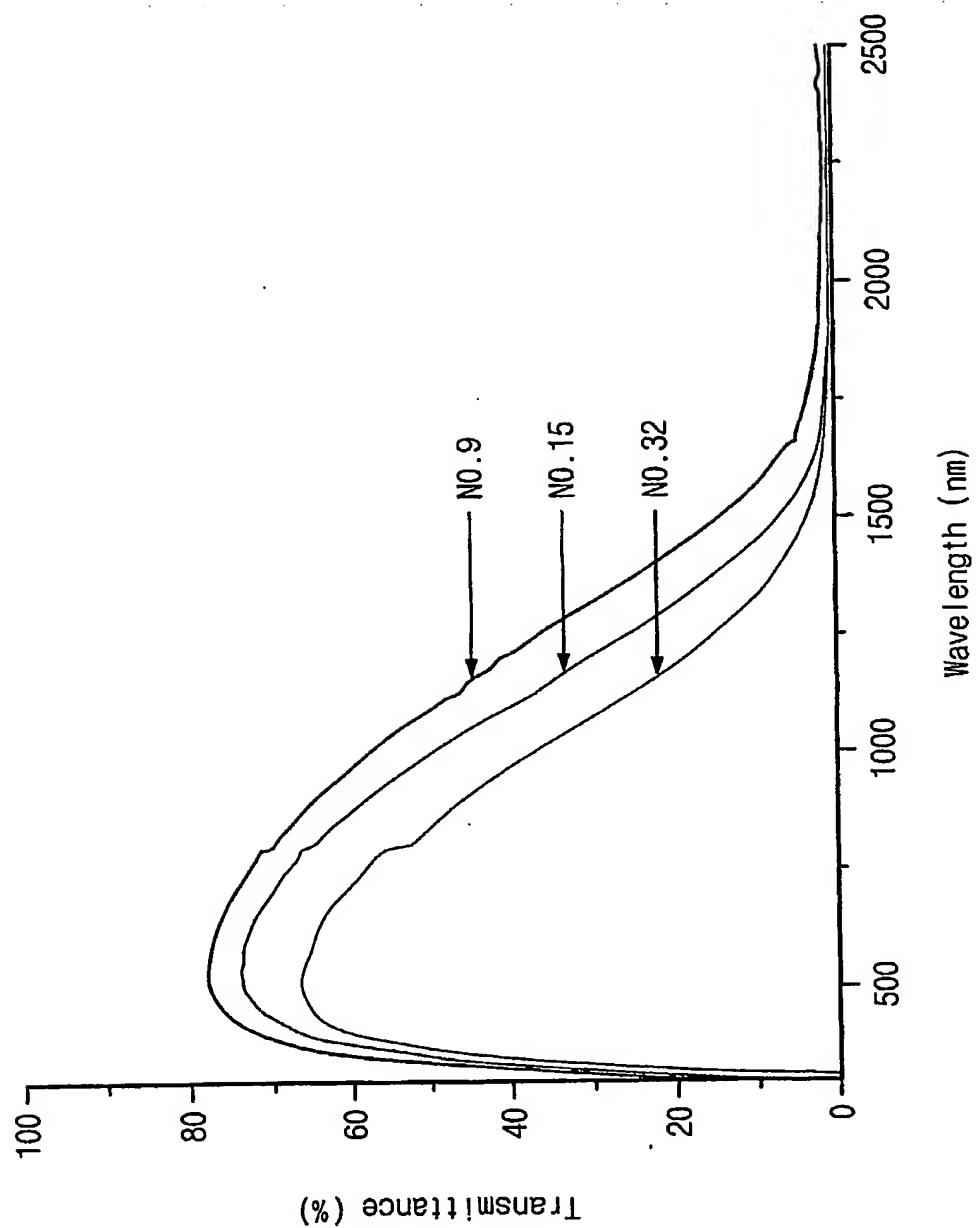


Fig. 3

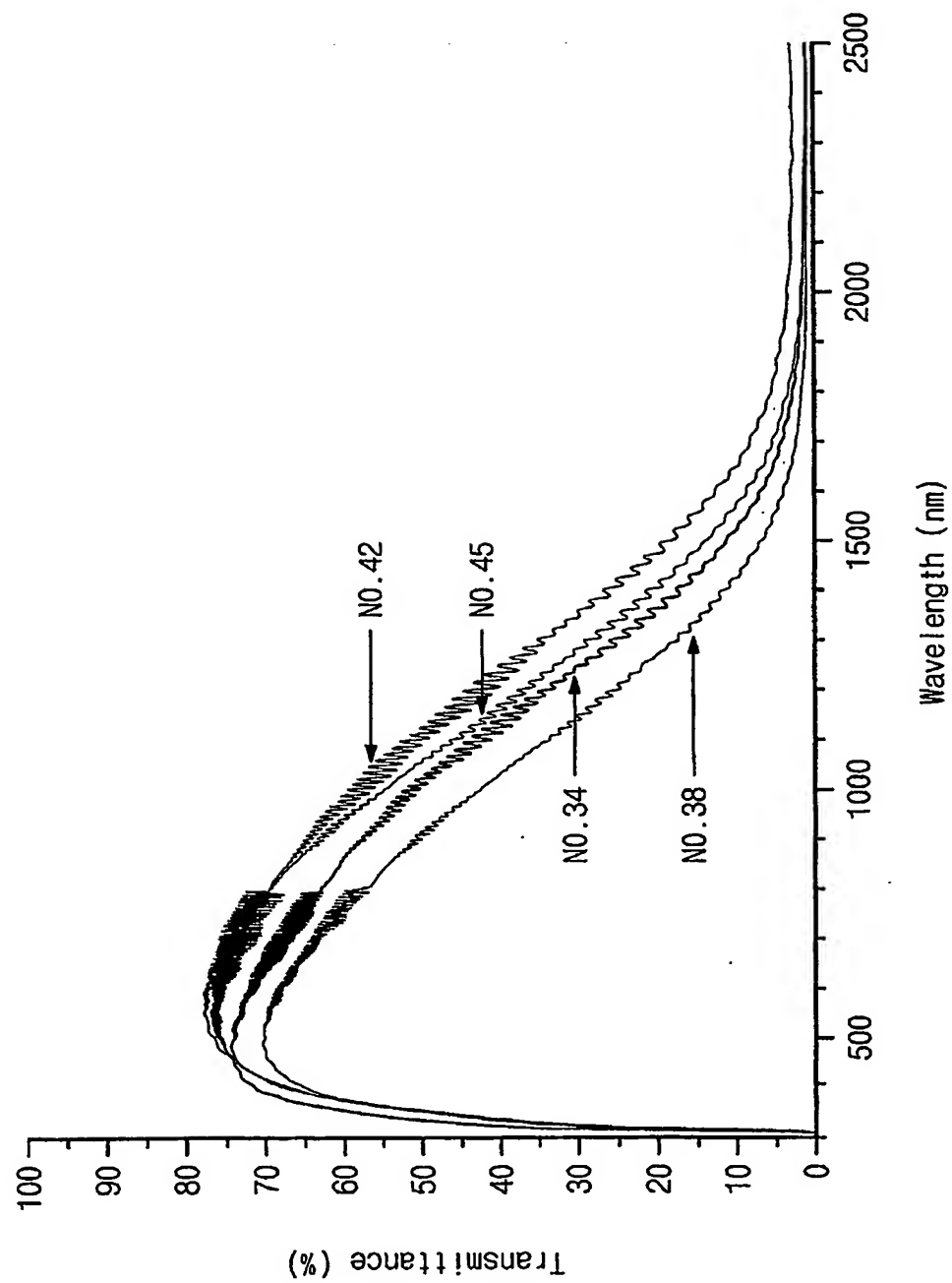


Fig. 4

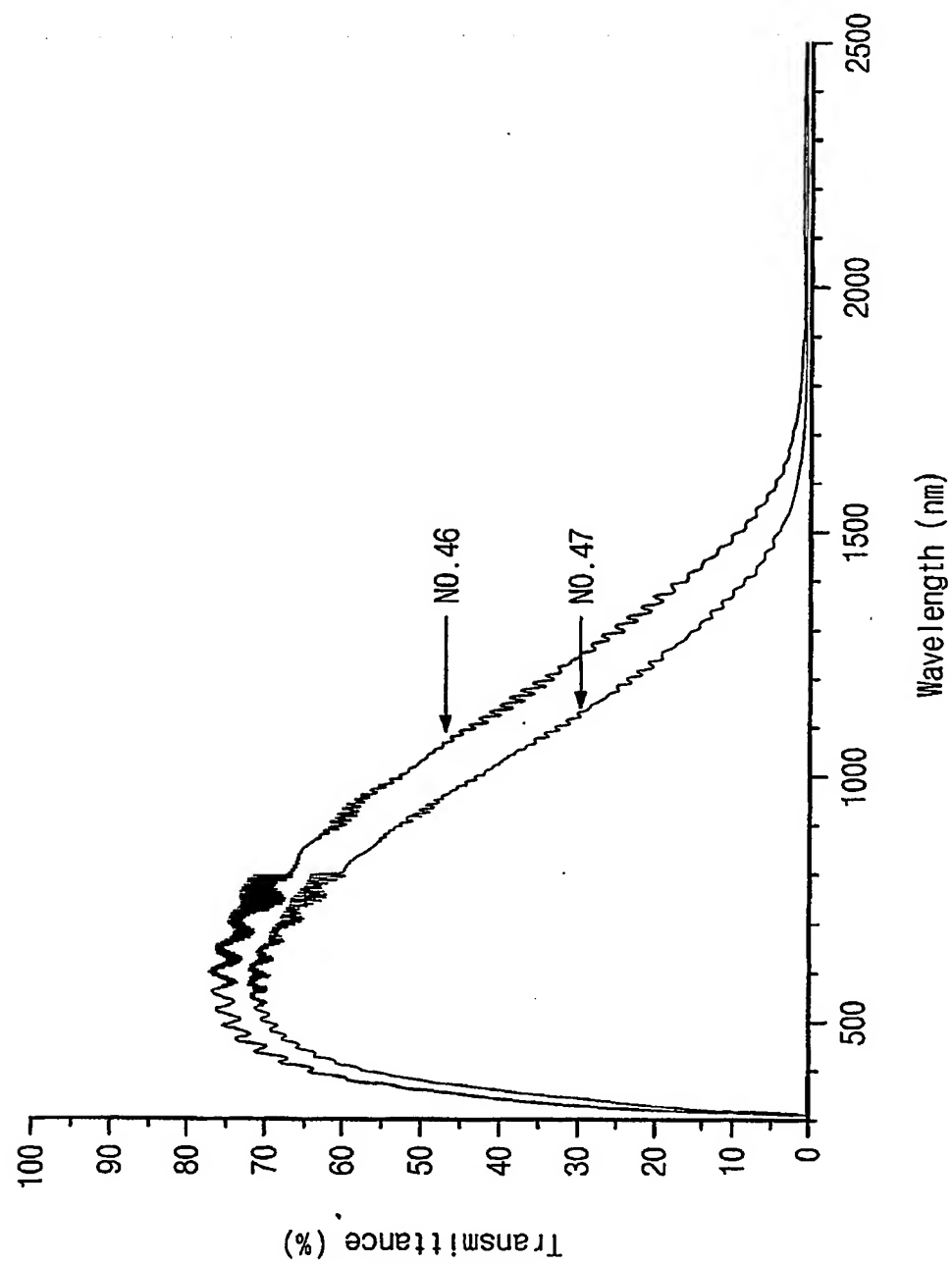
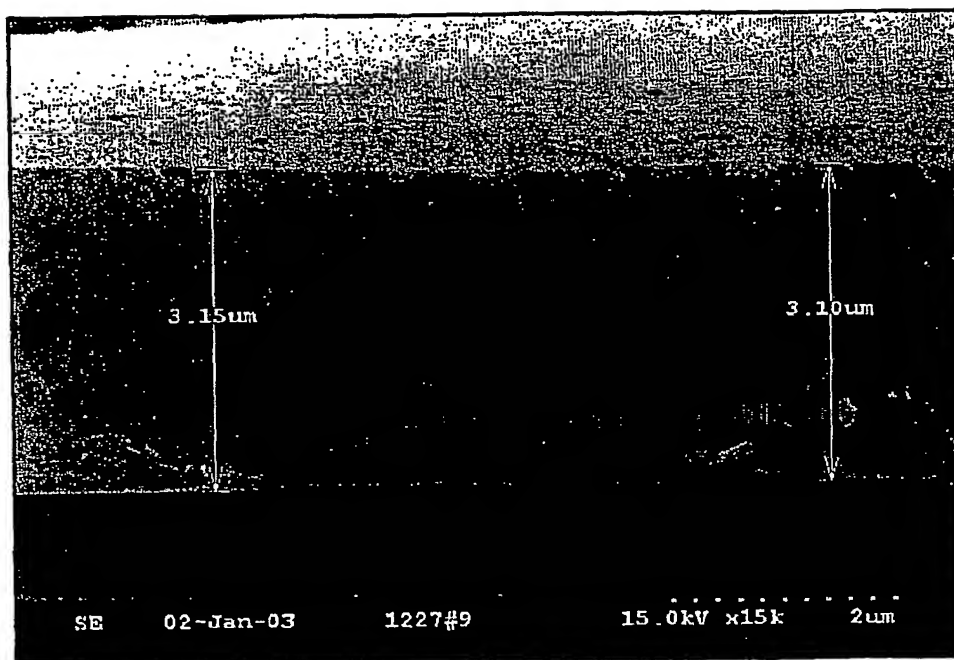


Fig. 5



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR03/00516

## A. CLASSIFICATION OF SUBJECT MATTER

**IPC7 C09D 5/00**

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09D 4/02, 5/24, B05D 7/02, H01J 32/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Korean Patent and applications for inventions since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NPS, PAJ, FPP, USP

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR-A-1999-41621(LG CHEMICAL CO.,LTD) 15.JUNE.1999 See the whole document	1 - 36
A	KR-A-2000-66670(LG CHEMICAL CO.,LTD) 15.NOVEMBER.2000 See the whole document	1 - 36
A	JP-A-1997-108621(NIPPON KAYAKU CO.,LTD) 28.APRIL.1997 See the whole document	1 - 36
A	JP-A-1997-316363(NIPPON KAYAKU CO.,LTD) 09.DECEMBER.1997 See the whole document	1 - 36
A	US-A-48067(Ji- Won Lee) 13.MARCH.2003 See the whole document	1 - 36

☐ Further documents are listed in the continuation of Box C.

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